Flow Phase Distribution of
Nitrogen and Phosphorus in the
Potomac River System

by

Roland C. Steiner, PhD, PE
Chief, Technical Services Unit

Interstate Commission on the Potomac River Basin
6110 Executive Boulevard, Suite 300
Rockville, Maryland 20852-3903

Report No. 86-4

April 1986

This report has been prepared by the Interstate Commission on the Potomac River Basin. Funds for this report are provided by the United States Government, the U.S. Environmental Protection Agency, and the signatory bodies to the Interstate Commission on the Potomac River Basin: Maryland, Pennsylvania, Virginia, West Virginia, and the District of Columbia. The opinions expressed are those of the author and should not be construed as representing the opinions or policies of the United States or any of its agencies, the several states, or the Commissioners of the Interstate Commission on the Potomac River Basin.

Flow Phase Distribution of Nitrogen and Phosphorus in the Potomac River System

Introduction

In an effort to improve prediction of nutrient delivery to the fall line on the Potomac River, nitrogen and phosphorus data are compared with storm flow and base flow for the total basin of the free flowing river and two upstream sub-basins. The motivation for this investigation is attributable to the emerging shift in aquatic nutrient abatement attention from point sources to non-point sources. As pollutant loads are reduced by improvements to sewage treatment plant (STP) and industrial discharges, the potential for further point source reduction diminishes. Attention is increasingly turning to non-point sources of pollution which impact the Tidewater Potomac and Chesapeake Bay.

Land use practices have been identified as significant contributors to concentrations of water-borne nutrients. However, analysis of erosion and sedimentation indicate that large amounts of sediment are stored in channels, river banks and flood plains. This stored sediment will be available for mobilization under normal flow patterns for years to come regardless of agricultural tillage methods in use now or adopted in the near future (Smith and Shoemaker, Shoemaker and Miller, and Schwartz). Many tillage practices now being promoted in order to reduce field erosion and nutrient runoff, do so by limiting the application of commercial and animal-derived fertilizer and by increasing infiltration. The objective of this investigation is to develop a comparison of nutrient concentrations between base flow and storm flow in different portions of the Potomac River Basin. The analysis is accomplished by performing the tasks of:

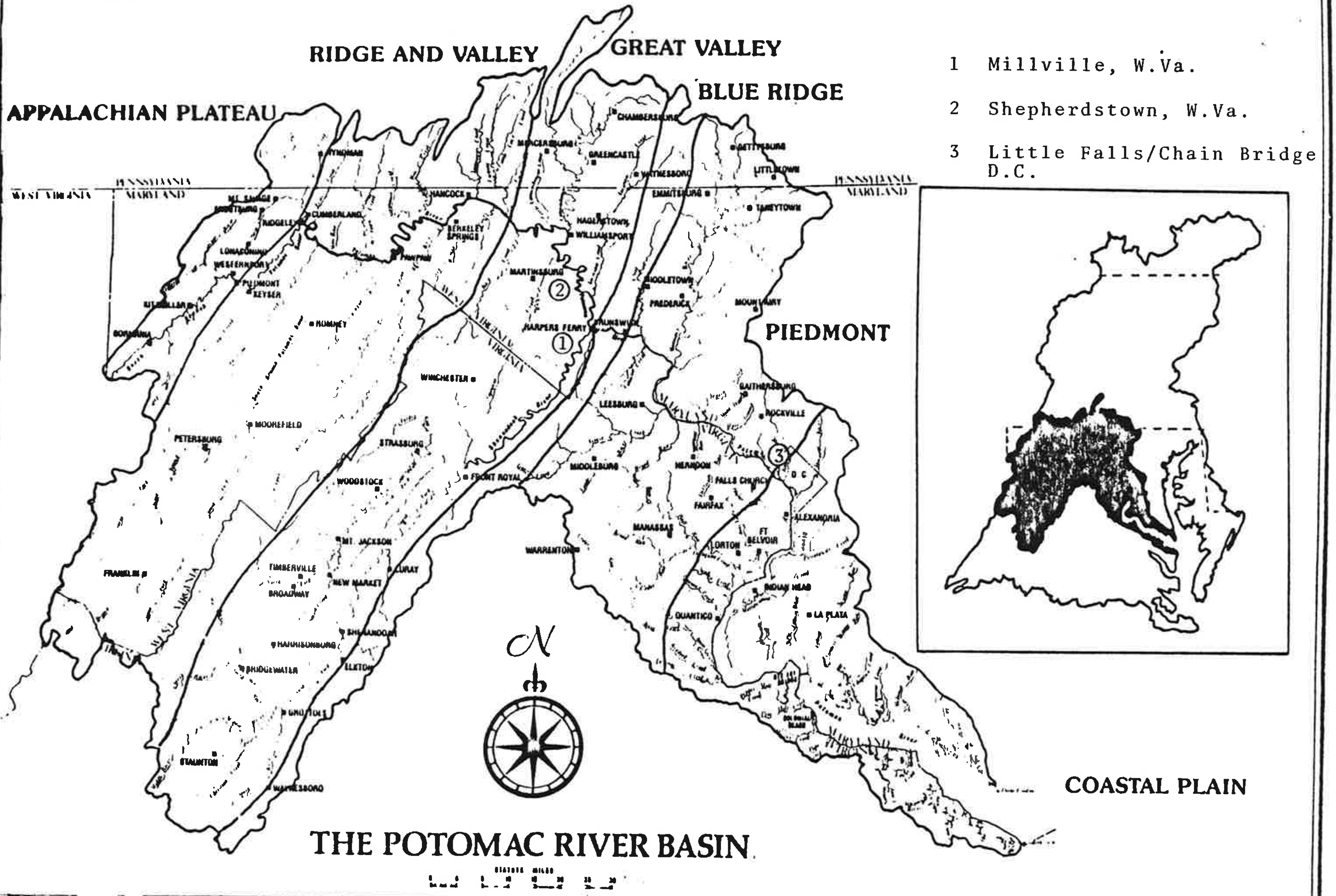
1. hydrograph separation into base flow and storm flow phases
2. regressing nutrient load on base flow and storm flow phases.

A map of the Potomac River Basin is given in Figure 1. It shows the mainstem and major tributaries, the gaging stations of interest in this study, the physiographic provinces and, the river's estuary and its position in the catchment of the Chesapeake Bay.

Hydrograph Flow Phase Separation

Daily stream flow data at Millville, W.Va. on the Shenandoah River, and Shepherdstown, W.Va. and Little Falls near Washington, D.C. on the Potomac were obtained for the period 1979 - 1983. The issue of hydrograph analysis is admittedly a combination of art and science. It has been examined and

FIGURE 1



1 Millville, W.Va.

2 Shepherdstown, W.Va.

3 Little Falls/Chain Bridge D.C.

characterized by many investigators (Hall, Freeze, Singh, Singh and Stall, Appleby, Chow, and Linsley, et al; to name just a few), and the consensus appears to favor logarithmic representation of both the rising and falling limbs of the hydrograph. Conceptual parallels have been drawn between flow recession and biological decay functions, heat transfer, and other natural processes. In addition, base flow recession has been compared with releases of water (which enters the hydrologic system as precipitation) from zones of ground storage.

In this analysis, the rising and falling limbs of the base flow hydrograph are represented by the following general mathematical expressions:

$B_{(t)} = B_{(t-1)} e^{a}$ for the rising limb

$B_{(t)} = B_{(t-1)} e^{-b}$ for the falling limb

where:

B = base flow phase value
t = time in days
e = exponential base
a = rising limb constant
b = falling limb constant.

A modifying factor is applied to the rising limb in order to smooth the shape of the hydrograph. The final form of the equation is:

$B_{(t)} = B_{(t-1)} e^{a(Favg/B_{(t)})}$ rising limb

where:

Favg = average of total flow on days (t) and (t-1).

Additionally, the falling limb is constrained such that if base flow is more than 70% of total flow, it is set to 80%. This algorithm has the effect of keeping the base flow near but below total flow during long recessions.

These equations and constraints produce a base flow hydrograph which behaves as expected in the general case, while relating it to the specific total flow hydrograph under consideration. The constants (a) and (b) are adjusted in order to produce a reasonable representation in the specific case. Opinions in the hydrologic community differ as to the exact shape and composition of the general base flow hydrograph; however, consistency of method is one of the important factors in hydrograph separation (Linsley, et al).

The rising and falling limb constants used to produce the base flow hydrographs are given in Figure 2. The resultant total flow and base flow hydrographs for the three gage sites are shown in Figures 3 - 5.

FIGURE 2 Base Flow Hydrograph Constants

	(a)	(b)
Shenandoah River at Millville, W.Va.	0.015	0.018
Potomac River at Shepherdstown, W.Va.	0.010	0.018
Potomac River at Little Falls nr D.C.	0.010	0.018

FIGURE 3

SHENANDOAH RIVER AT MILLVILLE, WEST VIRGINIA
Total and Base Flow (cfs)
For the Period 1979 - 1983

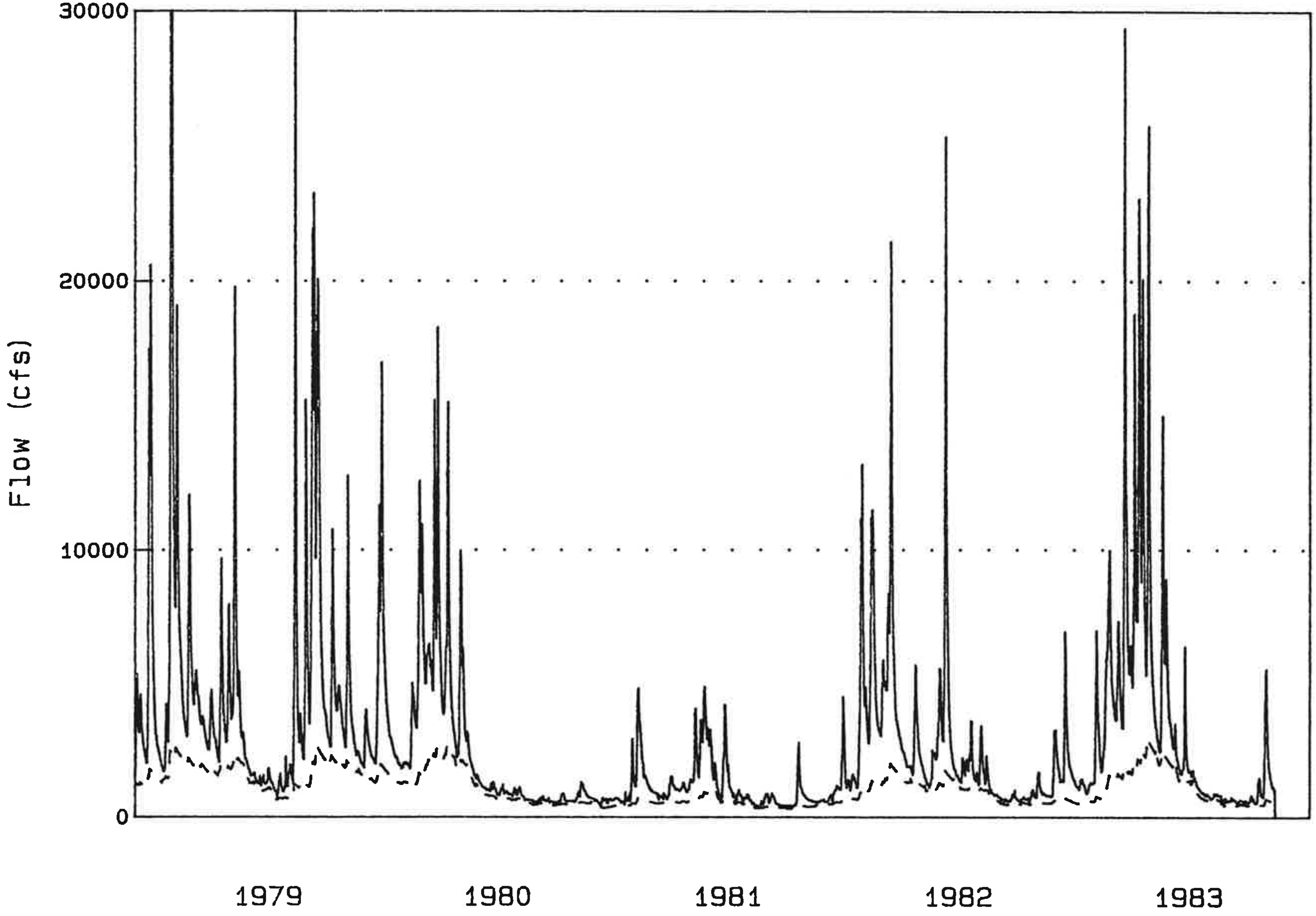


FIGURE 4

POTOMAC RIVER AT SHEPHERDSTOWN, WEST VIRGINIA
Total and Base Flow (cfs)
For the Period 1979 - 1983

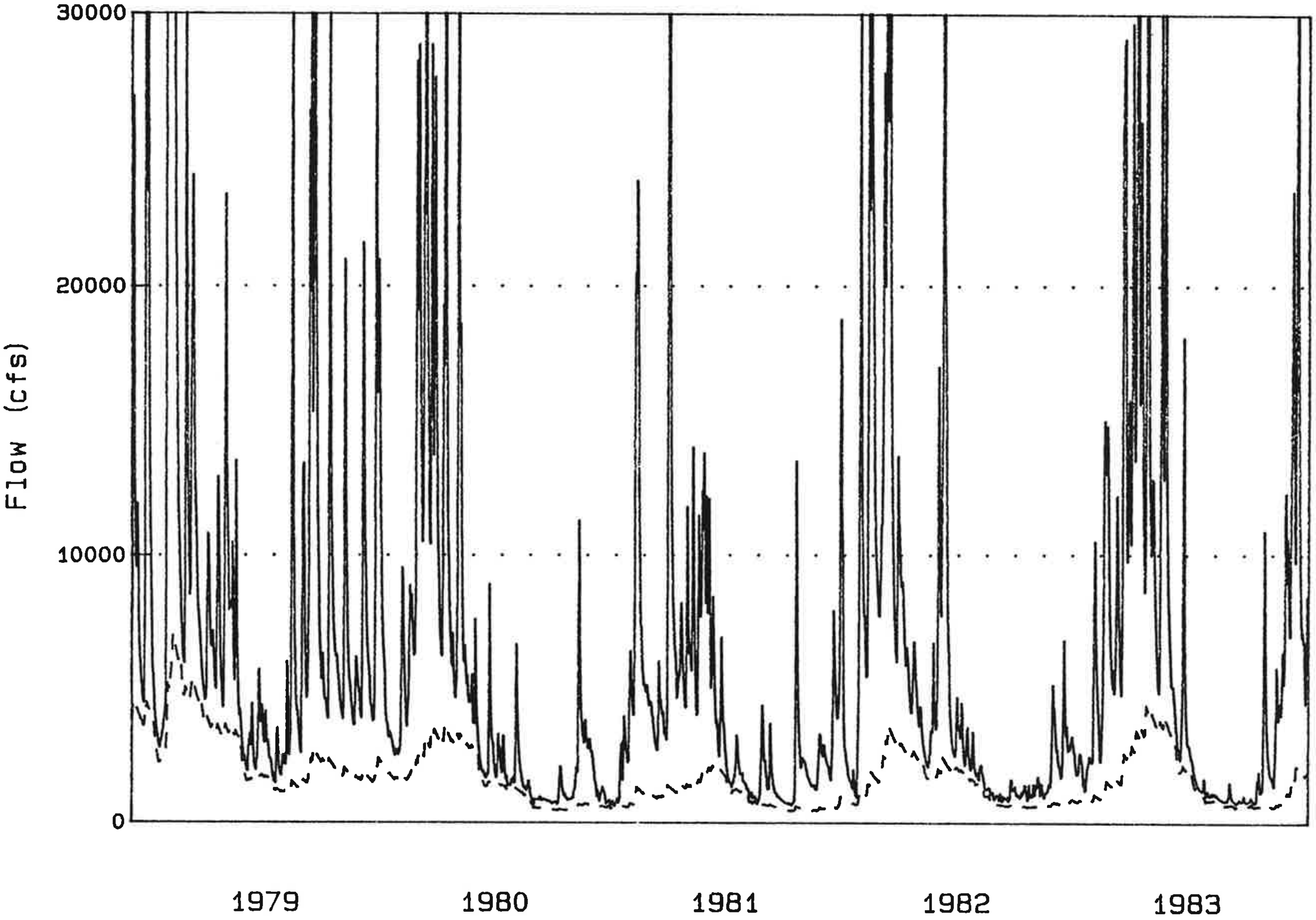
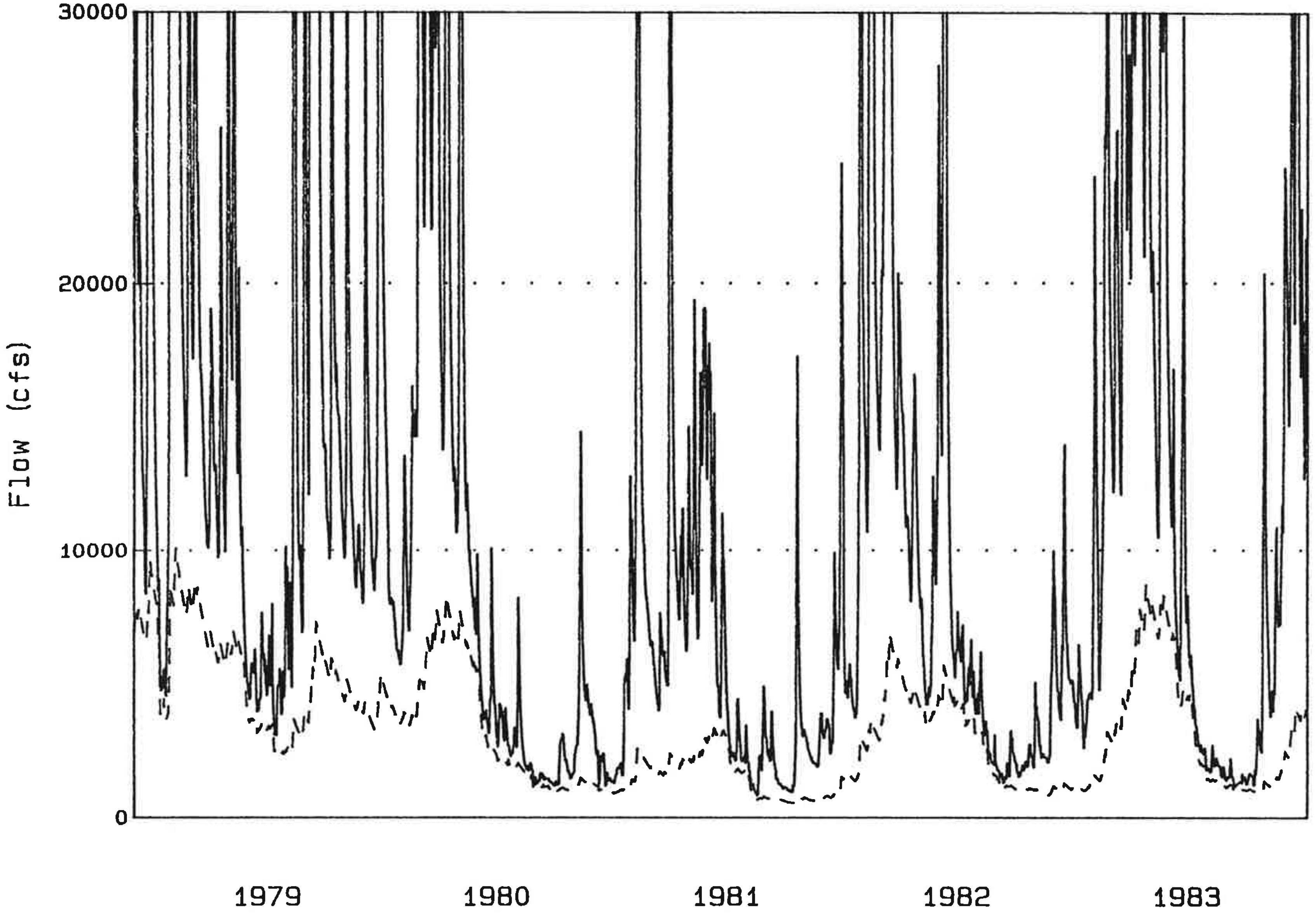


FIGURE 5

POTOMAC RIVER AT LITTLE FALLS, NEAR WASHINGTON, D.C.
Total and Base Flow (cfs)
For the Period 1979 - 1983



Flow separation and nutrient load estimation performed by the Metropolitan Washington Council of Governments (Schueler, Chittenden) is based on characterizing a day's flow as either storm or base flow. Whereas, this work partitions each day's flow into portions of the two phases.

Nutrient Data

Nutrient sampling data were readily available for stations at Millville, W.Va. on the Shenandoah River, and Shepherdstown, W.Va. and Chain Bridge at Washington, D.C. on the Potomac River. The Chain Bridge water quality sampling station is sufficiently close to the Little Falls flow gaging station as to avoid any significant problems due to intervening flow when the data from the two stations are used conjunctively in regression analysis. Data sets for consistent time periods at each of the stations cover the calendar years 1979 - 1983. Two forms each of nitrogen and phosphorous data are used in the analysis:

Total Nitrate,	TNO3	(mg/l as N)
Dissolved Nitrate,	DNO3	(mg/l as N)
Total Phosphorus,	TP	(mg/l as P)
Dissolved Phosphorus,	DP	(mg/l as P)

These nutrient data were made available by the U.S. Geological Survey Headquarters, Reston, Va., and were developed as part of the National Stream Quality Accounting Network (NASQAN) program.

Regression Analysis

In order to examine the relative contributions of storm flow and base flow, linear regressions are developed which relate nutrient load to flow. The flow phase distributions of nitrogen and phosphorus are examined for the two upper basin stations: Millville, W.Va. and Shepherdstown, W.Va., and the Chain Bridge fall line station at Washington, D.C.

Simple and multiple linear regressions are developed on the MINITAB computerized statistical package. In order to determine if there is any improvement in explained variance, regressions of nutrient load on total flow are developed and compared with those developed for storm flow and base flow. In addition, regressions are developed with a constant term in order to allow the meaningful computation of adjusted coefficients of determination ($\bar{r}2$). Thus, for each nutrient at each sampling station, 4 regressions are developed. The results are presented in Figures 6 - 8.

An examination of these results provides some insight into aquatic nutrient dynamics in the Potomac River system. In most cases, the constant term of the equation has a very low T-ratio (coefficient/standard deviation of coefficient) indicating a low

FIGURE 6

Shenandoah River at Millville, W.Va. Regression Coefficients
()'s indicate T-ratio; Coefficient/S.D. Coefficient

Parameter Load	No. Obs.	Con- stant	Total Flow	Storm Flow	Base Flow	Std. Error	$\bar{r}^2$
TNO_3	28	-647 (-1.0)	1.37 (7.2)			2023	65.4
	28		1.22 (10.8)			2023	
	28	-242 (-0.3)		1.59 (5.3)	0.89 (1.6)	2027	65.2
	28			1.59 (5.4)	0.76 (2.2)	1991	
DNO_3	28	-333 (-1.0)	1.22 (11.0)			1121	81.5
	28		1.33 (16.4)			1120	
	28	-302 (-0.8)		1.24 (7.3)	1.18 (3.6)	1142	80.8
	28			1.23 (7.3)	1.00 (4.4)	1133	
TP	37	-81.5 (-1.7)	0.18 (11.6)			170	78.6
	37		0.16 (16.8)			174	
	37	-46.9 (-0.9)		0.20 (8.4)	0.13 (3.1)	168	79.0
	37			0.20 (8.4)	0.10 (3.6)	168	
DP	38	-5.0 (-0.2)	0.08 (7.7)			126	61.0
	38		0.08 (12.9)			124	
	38	39.3 (1.0)		0.11 (6.8)	0.02 (0.7)	119	64.8
	38			0.11 (6.8)	0.04 (2.1)	119	

FIGURE 7

Potomac River at Shepherdstown, W.Va. Regression Coefficients
()'s indicate T-ratio; Coefficient/S.D. Coefficient

Parameter Load	No. Obs.	Con-stant	Total Flow	Storm Flow	Base Flow	Std. Error	$\bar{r}2$
TNO_3	27	163	0.93			1611	85.5
		(0.3)	(12.7)				
	27		0.95			1584	
			(22.1)				
	27	904		1.03	0.38	1524	87.0
		(1.5)		(12.2)	(1.3)		
	27			1.05	0.69	1559	
				(12.4)	(3.6)		
DNO_3	29	-216	1.16			2757	79.8
		(-1.0)	(11.0)				
	29		1.14			2709	
			(16.0)				
	29	1547		1.39	0.67	2582	82.3
		(1.4)		(9.4)	(0.8)		
	29			1.36	0.28	2628	
				(9.2)	(0.5)		
TP	39	148	0.04			397	15.3
		(1.4)	(2.8)				
	39		0.06			402	
			(6.3)				
	39	252		0.06	-0.04	393	17.0
		(1.9)		(3.1)	(-0.6)		
	39			0.06	0.05	407	
				(3.4)	(1.1)		
DP	38	114	0.01			241	2.9
		(1.7)	(1.4)				
	38		0.03			248	
			(4.6)				
	38	119		0.02	-0.05	234	8.7
		(2.5)		(2.2)	(-1.4)		
	38			0.03	0.02	251	
				(6.7)	(0.6)		

FIGURE 8

Potomac River at Little Falls (flow) and Chain Br. (parameter)
Regression Coefficients
()'s indicate T-ratio; Coefficient/S.D. Coefficient

Parameter Load	No. Obs.	Con-stant	Total Flow	Storm Flow	Base Flow	Std. Error	$\bar{r}2$
TNO$_3$	46	4484 (3.2)	0.95 (25.1)			8090	93.3
	46		1.02 (28.7)			8878	
	46	1232 (0.6)		0.91 (19.9)	2.03 (3.5)	7879	93.6
	46			0.90 (20.4)	2.29 (6.7)	7816	
DNO$_3$	63	-469 (-0.3)	1.34 (18.1)			8704	84.1
	63		1.32 (23.2)			8642	
	63	1116 (0.6)		1.41 (13.8)	0.55 (0.8)	8687	84.1
	63			1.40 (14.0)	0.85 (1.9)	8638	
TP	68	-2218 (-4.1)	0.36 (19.9)			3919	85.4
	68		0.32 (18.3)			4360	
	68	444 (0.6)		0.41 (21.0)	-0.70 (-3.0)	3439	88.8
	68			0.41 (21.5)	-0.59 (-4.2)	3422	
DP	64	-158 (-1.6)	0.05 (17.5)			682	82.9
	64		0.05 (18.9)			691	
	64	235 (1.6)		0.06 (17.3)	-0.10 (-2.3)	626	85.5
	64			0.06 (17.2)	-0.04 (-1.5)	635	

level of confidence in it being significantly different from zero. This is a favorable result from which it may be concluded that most of the variation in nutrient load is explained by variation in flow. The dimensional unit of the flow term coefficients is concentration in mg/l. This is an obvious aid in the interpretation of the results.

In most cases, the apparent nutrient concentration in the storm flow phase is more than that in the base flow phase; often twice as much. This finding, by itself, should have important implications in the programs aimed at aquatic nutrient abatement. The negative coefficients of base flow phosphorus at Shepherdstown and Chain Bridge have no plausible physical basis, and indicate that the flow phase separation and/or form of the model (linear regression) may not be the most appropriate (Woolhiser).

An unexpected and disappointing result is that the adjusted coefficient of determination ($\bar{r}2$) does not improve when total flow is partitioned into storm flow and base flow. Thus, flow phase separation has no appreciable effect on the explanatory power of flow as a predictor of nutrient load.

With the indication that storm flow is relatively richer in nutrients than base flow, and given the relative volumes of these flows over the 5-year period of analysis, a flow phase load comparison can be made. Figure 9 presents the ratios of storm flow load to base flow load of TNO3 and TP for the 3 sampling stations. Even though the hydrograph separation technique may not produce an exact representation of reality, and some assumptions of multiple linear regression theory may not be strictly met by the data, the results show that storm flow may contribute up to 4.5 times the nutrient load than that of base flow. This finding indicates that it may be the high intensity/low frequency events which carry the greatest proportion of nutrients and should be the focus of abatement programs. In addition, fixed frequency water quality sampling programs may lead to a systematically biased representation of true water quality. A program designed to sample equal volumes of flow may give more realistic results.

FIGURE 9

Comparison of Nutrient Loads in Storm Flow and Base Flow

Ratio of Nutrient Loads in Storm Flow and Base Flow for the Period 1979 - 1983

Shenandoah at Millville, W.Va.		Potomac at Shepherdstown, W.Va.		Potomac at Little Falls	
TNO3	TP	TNO3	TP	TNO3	TP
3.0	2.9	4.5	3.5	1.1	2.0

Caution, however, should be exercised in the use of these results on a time scale of less than a year. For the load ratio comparisons given in Figure 9, daily nutrient load values are developed for a five-year period using a least squares linear regression on only 30 to 40 observations for the upper basin stations and only 50 to 60 observations for the fall line. No seasonal characteristics were accounted for in the analysis; whereas, an examination of the resultant estimated monthly loadings of TNO3 and TP at Chain Bridge for the year 1983 reflect the dominance of base flow in the summer, see Figure 10. The negative loadings of TP in the summer indicate a deficiency in the simple flow phase nutrient model derived from sparse year-round data. Stratified and modified stratified flow based monthly estimates (Schueler, Chittenden) are provided in Figure 10 for a comparison of results derived by the different methods. Both Schueler and Chittenden developed winter/summer seasonal nutrient concentrations for use in their estimation algorithms.

The arrival of nutrients in a particular storm flow wave at the Chain Bridge fall line monitoring station precedes the arrival of most of the nutrients mobilized by rainfall on a distant upstream watershed. This is so, because wave speed (celerity) in river systems is approximately 1.5 times faster than the velocity of the water itself (Linsley, et al). Thus, the increase in nutrient concentration at the fall line with increase in flow is likely due to resuspension of sediment stored in and near the channel (Schwartz) and mobilization of associated nutrients. A further confounding issue involves the size and complexity of the Potomac basin above the fall line; base flow at Chain Bridge may contain storm flow from some distant upstream sub-basin(s).

FIGURE 10

Estimated Monthly Nutrient Loadings at Chain Bridge
for the Year 1983
(millions of lbs)

	Nitrogen			Phosphorus		
		OXN(2)			TP(2)	
	TNO3(1)	SF	MSF	TP(1)	SF	MSF
January	0.92	0.87	0.99	0.11	0.09	0.08
February	2.55	3.22	3.41	0.69	0.49	0.43
March	4.66	5.78	6.14	1.12	0.78	0.71
April	8.55	10.59	10.68	2.10	1.83	1.83
May	5.46	5.00	5.44	0.42	0.64	0.63
June	2.85	2.31	2.50	-0.15	0.24	0.28
July	1.19	0.63	0.69	-0.22	0.06	0.07
August	0.60	0.28	0.26	-0.09	0.04	0.04
September	0.46	0.25	0.24	-0.08	0.03	0.03
October	1.00	0.88	0.83	0.15	0.09	0.13
November	1.81	2.16	2.10	0.39	0.30	0.52
December	4.82	6.52	7.03	1.23	0.99	1.06
1983 Total	34.87	38.49	40.31	5.67	5.58	5.81

(1) Loads estimated from regressions of load on storm flow and base flow as described in this paper.

(2) Loads estimated by Schueler and Chittenden. OXN = total nitrite + nitrate. Stratified Flow method (SF) and Modified Stratified Flow method (MSF).

As an alternate analysis, ln(nutrient load) is regressed on ln(total flow). For all but DNO3, TP and DP at Shepherdstown, and DNO3 at Chain Bridge, the previously described regressions explain more variation in nutrient load than do ln-ln regressions. The derived coefficients of the ln-ln regressions are presented in Figures 11-13.

FIGURE 11

Shenandoah River at Millville, W.Va.

ln(nutrient load)-ln(total flow) Regression Coefficients
()'s indicate T-ratio; Coefficient/S.D. Coefficient

Parameter ln Load	No. Obs.	Constant	ln Total Flow	Std. Error	$\bar{r}$2
TNO$_3$	28	-2.68 (-1.60)	1.32 (6.02)	0.985	56.6
	28		0.97 (38.65)	1.013	
DNO$_3$	28	-1.44 (-0.89)	1.16 (5.41)	0.977	51.1
	28		0.97 (39.62)	0.973	
TP	37	-2.06 (-2.83)	1.00 (10.33)	0.477	74.6
	37		0.73 (64.09)	0.522	
DP	38	-2.65 (-2.20)	0.99 (6.23)	0.810	50.6
	38		0.64 (35.26)	0.851	

FIGURE 12

Potomac River at Shepherdstown, W.Va.

ln(nutrient load)-ln(total flow) Regression Coefficients
()'s indicate T-ratio; Coefficient/S.D. Coefficient

Parameter ln Load	No. Obs.	Constant	ln Total Flow	Std. Error	$\bar{r}2$
TNO_3	28	0.38 (0.56)	0.95 (11.86)	0.320	83.8
	28		0.99 (139.62)	0.316	
DNO_3	28	-0.10 (-0.17)	1.02 (14.37)	0.341	88.0
	28		1.00 (133.49)	0.335	
TP	37	-1.25 (-1.11)	0.81 (5.96)	0.693	47.6
	37		0.66 (49.33)	0.695	
DP	38	-0.22 (-0.18)	0.61 (4.09)	0.747	29.8
	38		0.58 (40.37)	0.737	

FIGURE 13

Potomac River at Little Falls (flow) and Chain Br. (parameter)

ln(nutrient load)-ln(total flow) Regression Coefficients
()'s indicate T-ratio; Coefficient/S.D. Coefficient

Parameter ln Load	No. Obs.	Constant	ln Total Flow	Std. Error	$\bar{r}2$
TNO$_3$	28	-1.37 (-2.41)	1.16 (18.82)	0.479	88.7
	28		1.01 (125.75)	0.504	
DNO$_3$	28	-2.76 (-4.53)	1.30 (18.74)	0.615	85.0
	28		0.99 (98.00)	0.704	
TP	37	-4.93 (-6.96)	1.27 (15.98)	0.747	79.1
	37		0.72 (54.17)	0.977	
DP	38	-3.77 (-5.66)	1.04 (13.94)	0.699	75.4
	38		0.62 (51.87)	0.854	

Conclusions

Flow phase regressions of nutrient load developed on sparse year-round data appear to lack important seasonal characteristics.

The regression of nutrient loads on storm flow and base flow phases of total flow in the Potomac River system indicated that storm flow is generally higher in nutrient concentration than base flow.

The regression of nutrient loads on storm flow and base flow phases of total flow in the Potomac River system makes no improvement over regressions developed on total flow as a single explanatory variable in the prediction of nutrient loads.

During a period of several years, storm flow carries up to 4.5 times the nutrient load carried in base flow.

Straight numerical regressions generally explain more variation in nutrient load than ln(nutrient)-ln(flow) regressions.

Fixed frequency water quality sampling programs may lead to a systematically biased representation of true water quality. A program designed to sample equal volumes of flow may give more realistic results.

Recommendations

The negative TP loadings indicated by the regressions for Chain Bridge in 1983 indicate that the specific flow phase separation and/or form of the model (linear regression) may not be the most appropriate for this application. The winter flow response to rainfall may be significantly different from that in the summer.

In general, the results and conclusions of this study should be considered by regulatory and legislative decision makers when developing non-point source nutrient abatement programs for application in the Potomac River system.

Extending this analysis to other sub-basins (e.g. the Monocacy River and Goose Creek) may provide similar aquatic nutrient information for those catchments. Seasonal characteristics should be included.

This analysis might be usefully extended by comparing estimated nutrient loadings for 1984 and 1985 with the more frequent sample observations taken during that more recent period. The frequency of more recent data may be sufficient to investigate nutrient hysteresis effects during rising and falling limbs of the hydrograph.

References

Appleby, F. Victor, 1970. Recession and the Baseflow Problem. Water Resources Research 6(5):1398-1403.

Chittenden, Wendy, 1985. Modification of the Stratified Flow Load Estimation Procedure and Estimation of 1984 Potomac Fall Line Loadings. Chain Bridge Fall Line Monitoring Station File. Metropolitan Washington Council of Governments. Washington, D.C.

Chow, Ven Te, Editor-in-Chief, 1964. Handbook of Applied Hydrology. McGraw-Hill Book Company, New York.

Freeze, R. Allan, 1972. Role of subsurface Flow in Generating Surface Runoff, 1. Base Flow Contributions to Channel Flow. Water Resources Research 8(3):609-623.

Freeze, R. Allan, 1972. Role of subsurface Flow in Generating Surface Runoff, 2. Upstream Source Areas. Water Resources Research 8(5):1272-1283.

Hall, Francis R., 1968. Base-Flow Recessions -- A Review. Water Resources Research 4(5):973-983.

Linsley, Ray K., Jr., Max A. Kohler and Joseph L.H. Paulus, 1958. Hydrology for Engineers. McGraw-Hill Book Company, Inc., New York.

Schueler, Thomas R., 1984. Chain Bridge Input Monitoring Data 1983/Calculation of Fall Line Pollutant Loadings. PEM Post-Audit File. Metropolitan Washington Council of Governments. Washington, D.C.

Schwartz, Stuart S., 1986. A Conceptual Sediment Transport Model for the Monocacy River Basin. Forthcoming paper.

Shoemaker, Leslie L. and Andrew J. Miller, 1986. Sediment Storage and Transport in the Mainstem Potomac River Between Point of Rocks and Seneca Dam. Forthcoming paper.

Singh, Krishan P., 1968. Some Factors Affecting Baseflow. Water Resources Research 4(5):985-999.

Singh, Krishan P. and John B. Stall, 1971. Derivation of Base Flow Recession Curves and Parameters. Water Resources Research 7(2):292-303.

Smith, James A. and Leslie L. Shoemaker, 1984. The Role of Sediment in Nonpoint Pollution in the Potomac River Basin. ICPRB Working Paper. Interstate Commission on the Potomac River Basin, Rockville, Maryland.

Woolhiser, David A., 1984. Comment on "Identifying Sources of Groundwater Pollution: An Optimization Approach" by Steven M. Gorelick, Barbara Evans, and Irwin Remson. Water Resources Research 20(6):743-744.